



Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number:

0 328 177
A2

⑫

EUROPEAN PATENT APPLICATION

⑬ Application number: 89200163.7

⑮ Int. Cl.4: C11D 17/00

⑭ Date of filing: 26.01.89

⑬ Priority: 10.02.88 GB 8803036

⑯ Applicant: UNILEVER NV
Burgemeester s'Jacobplein 1 P.O. Box 760
NL-3000 DK Rotterdam(NL)

⑭ Date of publication of application:
16.08.89 Bulletin 89/33

⑭ CH DE ES FR IT LI NL SE

⑬ Designated Contracting States:
CH DE ES FR GB IT LI NL SE

Applicant: UNILEVER PLC
Unilever House Blackfriars P.O. Box 68
London EC4P 4BQ(GB)

⑭ GB

⑯ Inventor: Machin, David
32 Brancote Road
Oxtor Birkenhead L43 6TJ(GB)
Inventor: van de Pas, Johannes Cornelis
Philips Willemstraat 6
NL-3136 CV Vlaardingen(NL)

⑯ Representative: Tan, Bian An, Ir. et al
Unilever N.V. Patent Division P.O. Box 137
NL-3130 AC Vlaardingen(NL)

⑮ Liquid detergents.

⑯ Improved flexibility in incorporation of soluble salts in structured aqueous liquid detergents is provided by incorporating a surfactant with a salting-out resistance greater than or equal to 6.4 and which has an average alkyl chain length greater than 6 C-atoms provided that the liquid yields substantially no clear liquid active rich layer upon centrifuging at 750G for 20 hours at 25°C. The salting-out resistance is the minimum amount in grams equivalent of trisodium nitrilotriacetate added to 1 litre of a 5% aqueous solution of the surfactant at room temperature, to achieve phase separation as evidenced by cloudiness.

EP 0 328 177 A2

LIQUID DETERGENTS

The present invention is concerned with liquid detergent compositions which contain sufficient detergent active material and sufficient dissolved electrolyte to result in a surfactant structure within the composition. Such compositions are sometimes referred to as 'internally structured' since the structure is due to primary ingredients rather than to secondary additives, such as certain cross-linked polyacrylates, which can be 5 added as 'external structurants' to a composition which would otherwise show no evidence of a structure.

Internal structuring is very well known in the art and may be deliberately brought about to endow properties such as consumer preferred flow properties and/or turbid appearance. Many internally structured liquids are also capable of suspending particulate solids such as detergency builders and abrasive particles. Examples of such structured liquids without suspended solids are given in US patent 4 244 840 whilst 10 examples where solid particles are suspended are disclosed in specifications EP-A-160 342; EP-A-38 101; EP-A-104 452 and also in the aforementioned US 4 244 840.

Some of the different kinds of surfactant structuring which are possible are described in the reference H.A.Barnes, 'Detergents', Ch.2. in K.Walters (Ed), 'Rheometry: Industrial Applications', J.Wiley & Sons, Letchworth 1980. In general, the degree of ordering of such systems increases with increasing surfactant 15 and/or electrolyte concentrations. At very low concentrations, the surfactant can exist as a molecular solution, or as a solution of spherical micelles, both of these being isotropic. With the addition of further surfactant and/or electrolyte, structured (anisotropic) systems can form. They are referred to respectively, by various terms such as rod-micelles, planar lamellar structures, lamellar droplets and liquid crystalline phases. Often, different workers have used different terminology to refer to the structures which are really 20 the same. The presence of a surfactant structuring system in a liquid may be detected by means known to those skilled in the art for example, optical techniques, various rheometrical measurements, x-ray or neutron diffraction, and sometimes, electron microscopy.

One common type of internal surfactant structure is sometimes referred to as a dispersion of lamellar droplets (lamellar dispersion) These droplets consist of an onion-like configuration of concentric bilayers of 25 surfactant molecules, between which is trapped water or electrolyte solution (aqueous phase). Systems in which such droplets are close-packed provide a very desirable combination of physical stability and solid-suspending properties with useful flow properties.

As used herein, the term electrolyte means any ionic water soluble material. However, in structured liquids, not all the electrolyte is necessarily dissolved but may be suspended as particles of solid because 30 the total electrolyte concentration of the liquid is higher than the solubility limit of the electrolyte. Mixtures of electrolytes also may be used, with one or more of the electrolytes being in the dissolved aqueous phase and one or more being substantially only in the suspended solid phase. Two or more electrolytes may also be distributed approximately proportionally, between these two phases. In part, this may depend on processing, e.g. the order of addition of components. On the other hand, the term 'salts' includes all organic 35 and inorganic materials which may be included, other than surfactants and water, whether or not they are ionic, and this term encompasses the sub-set of the electrolytes (water soluble materials).

The amounts and types of surfactants and salts (e.g. builders, buffers, enzyme stabilizers, anti-corrosives) which ideally one would want to incorporate in such systems, will vary a great deal according to the type of product being incorporated. Unfortunately, this is hampered in some cases, by incompatibility of 40 components and one of the ways in which this can manifest itself is salting-out (precipitation) of the surfactants due to the salts present. This is particularly a problem where one or both of the salt and surfactant concentrations is relatively high, although the precise onset of salting-out will depend on the nature of the materials in question. It is often (but not exclusively) a problem when the salts contain a high proportion of electrolyte.

45 This has given rise to a desire to identify surfactants and surfactant blends which can stably be incorporated in such liquids to endow an improved degree of tolerance of a wide range of types and concentrations of salts. This is essentially the problem addressed in patent specification EP-A-178,006, although the surfactants described there for this purpose (alkyl polycarboxylates) do not give the degree of electrolyte tolerance which the present invention seeks to provide.

50 Since many of the usual salts are also electrolytes, one may assume that suitable surfactants to give the required improvement could be identified by dissolving them in water and testing their tolerance to progressively increasing amounts of added electrolyte. Unfortunately, we have found that this is not always an accurate predictor. The reason could be due to the fact that an aqueous solution of surfactant will be a molecular solution or a solution of spherical micelles. This is quite different to the arrangement of the surfactant molecules in structured liquids. Thus, as electrolyte is progressively added to molecular or

spherical micelle solutions of surfactant, the behaviour of the surfactant will not always mimic that in the structured systems.

However, it has now been found that unexpectedly, especially suitable surfactants (hereinafter called 'stabilising surfactants') can be identified using a test of the general kind referred to above, provided that it is framed in a suitable manner, provided that one defines an appropriate threshold for deciding whether a particular surfactant passes the test and provided one also ensures that the composition containing the stabilising surfactant gives a certain result upon centrifugation. This provides the advantage that the surfactants may be screened for use in novel internally structured detergent liquids.

The test herein prescribed for electrolyte tolerance is termed the measurement of salting-out resistance. 10 For this test, 200ml is prepared of a 5% by weight aqueous solution of the surfactant in question. Trisodium nitrolotriacetate (NTA) is added at room temperature (ca 25 °C) until phase separation, as observed by the onset of cloudiness, occurs. The amount of NTA added at this point, as expressed in gram equivalents added to 1 litre of the surfactant solution (1 mol of NTA = 3 equivalents) is the salting-out resistance of the surfactant. Where convenient, the abbreviation SOR will be used for salting-out resistance.

15 Thus, the present invention provides an aqueous liquid detergent composition comprising detergent active material and dissolved electrolyte in amounts sufficient to result in a surfactant structure within said composition, which composition yields substantially no clear liquid active rich layer upon centrifuging at 750G for 20 hours at 25 °C, wherein the detergent active material comprises a stabilising surfactant, which has an average alkyl chain length greater than 6 carbon atoms, and which has a salting-out resistance (as 20 hereinbefore defined), greater than, or equal to 6.4.

25 As compared with previously known surfactant structured liquid detergents, the selection of surfactants as described above allows the compositions of the present invention to be capable of greater flexibility in the incorporation of large amounts of salts, especially soluble salts (i.e. electrolytes) and improved possibilities for the incorporation of polymer builders, especially water-soluble builders, which can also act to bring about a desirable viscosity reduction in the product. The incorporation of higher levels of 30 surfactants is advantageous for fatty soil removal. In particular, where the stabilising surfactant is nonionic in character, the ensuing incorporation of high levels of nonionic rather than anionic surfactant is advantageous for the stability of any enzymes present, these in general being more sensitive to anionics than to nonionics. In general, the applicants have observed a trend that the higher the measured SOR, the lower is the concentration of surfactant necessary to achieve a given advantage.

For a composition to be in accordance with the present invention, it is not only necessary for it to contain at least some stabilising surfactant as hereinbefore defined but also for the compositions as a whole to yield substantially no clear liquid active rich layer upon centrifugation at 750G for 20 hours at 25 °C. The abbreviation G refers to the value of the earth's normal gravitational force. It should be noted that this 35 requirement excludes compositions which do not demonstrate the advantage provided by compositions of the present invention and also those compositions which are the subject of our co-pending patent application, reference no.C.3218, entitled 'Aqueous Detergent Compositions and Methods of Forming Them' filed on the same day as this application.

In this context, the term 'clear' in respect of liquid active rich layer means totally or substantially clear 40 to the unaided eye. A liquid layer which is not active rich will contain less than 10% by weight of surfactant (detergent active) material, preferably less than 5%, most preferably less than 2% by weight.

The stabilising surfactant may constitute all or part of the detergent active material. The only restriction on the total amount of detergent active and electrolyte is that together they must result in formation of a structuring system. Thus, within the ambit of the present invention, a very wide variation in surfactant types 45 and levels is possible. The selection of surfactant types and their proportions, in order to obtain a stable liquid with the required structure will, in the light of the present teaching, now be fully within the capability of those skilled in the art. However, it can be mentioned that an important sub-class of useful compositions is those where the detergent active material comprises one or more conventional or 'primary' surfactants, together with one or more stabilising surfactants. Typical blends useful for fabric washing compositions 50 include those where the primary surfactant(s) comprise nonionic and/or a non-alkoxylated anionic and/or an alkoxylated anionic surfactant.

The stabilising surfactant should have an average alkyl chain length greater than 6 carbon atoms, it is usually preferred that the stabilising surfactant have an average alkyl chain length greater than 8 carbon atoms. Some especially preferred classes of stabilising surfactants which may be used alone or in 55 combination are:-
alkyl polyalkoxylated phosphates;
alkyl polyalkoxylated sulphosuccinates;
dialkyl diphenyloxide disulphonates; and

alkyl polysaccharides (sometimes called alkyl polyglucosides or polyglycosides).

A wide variety of such stabilising surfactants is known in the art, for example the alkyl polysaccharides described in European patent specification nos. EP-A-70 074; 70 075; 70 076; 70 077; 75 994; 75 995; 75 996 and 92 355.

5 Especially preferred are those stabilising surfactants (of whatever chemical type) which have an SOR greater than 9.0.

In many (but not all) cases, the total detergent active material may be present at from 2% to 50% by weight of the total composition, especially from 5% to 35% and most preferably from 10% to 30% by weight. Thus, these figures will apply both to blends of primary and stabilising surfactants, as well as to the 10 case where the detergent active material consists entirely of stabilising surfactant. However, with blends of primary and stabilising surfactants, the amount of stabilising surfactant material will typically constitute from 0.1% to 45% by weight of the total composition, especially from 0.5% to 30% and most preferably from 1% to 30% by weight. In such blends, the stabilising surfactant will often constitute from 5% to 90% by weight of the total detergent active material, especially from 7.5% to 90% and most preferably from 10% to 90% 15 by weight.

Generally, it is very desirable that the compositions should have a rheology and a minimum stability, compatible with most commercial and retail requirements. For this reason, we generally prefer the compositions of the present invention to yield no more than 2% by volume phase separation upon storage at 25 °C for 21 days from the time of preparation and to have a viscosity of no greater than 2.5 Pas, 20 preferably 1 Pas at a shear rate of 21 s⁻¹.

In the case of blends of primary and stabilising surfactants, the precise proportions of each component which will result in such stability and viscosity will depend on the type(s) and amount(s) of the electrolytes, as is the case with conventional structured liquids. Thus, by way of illustration, Figure 1 shows a schematic representation of a typical ternary stability diagram for a blend of dodecyl benzene sulphonate (DoBS), a 25 C₁₂₋₁₅ fatty alcohol ethoxylated with an average of 7 moles of ethylene oxide, and a stabilising surfactant. Locus I illustrates the boundary of compositions which are stable at one electrolyte level (say 10% by weight). For this boundary, the broken lines A, B, C have the following meanings

A = Minimum weight fraction of stabilising surfactant with respect to the total surfactant level, to obtain a stable liquid detergent composition (here 0.06).

30 B = Maximum weight fraction of ethoxylated fatty alcohol with respect to the total surfactant level, which can stably be incorporated (here 0.34).

C = Minimum weight fraction of charged surfactant with respect to the total surfactant level (here 0.37), to obtain a stable liquid detergent composition (assuming the stabilising surfactant is nonionic in type).

35 Locus II shows the same boundary at a higher electrolyte level (say 12.5% by weight). Thus, it can be appreciated that when determining compositional parameters at different electrolyte levels, it is necessary to change the proportions of surfactants so that the test composition is always effectively in the same place relative to the stability boundary. Such adjustments similarly have to be made in determining the threshold 40 levels A, B and C at different electrolyte levels, as will be shown hereinbelow by way of example.

In such ternary surfactant blends, the use of a stabilising surfactant as a co-surfactant together with one or more primary surfactants leads to a larger stable area within the stability diagram (i.e. a wider range of surfactant ratios result in stable compositions) than would be expected from the additive behaviour of the respective binary combinations. Figure 2 represents a system of 23% total surfactant, 10% sodium citrate 45 and 67% water, the surfactants being dodecyl benzene sulphonate, C₁₂₋₁₅E₇ and the stabilising surfactant C₁₂₋₁₃G₃ (see key at end of Example 1). Ternary diagram a) shows the expected additive behaviour from the binary systems whilst diagram b) shows the stability area found in practice. N.B. In these diagrams, numbers along the axes denote the fraction of surfactant with respect to the total surfactant in the composition.

50 The detergent active material in general, may comprise one or more surfactants, and whether in the primary or stabilising categories, may be selected from anionic, cationic, nonionic, zwitterionic and amphoteric species, and (provided mutually compatible) mixtures thereof. For example, they may be chosen from any of the classes, subclasses and specific materials described in 'Surface Active Agents' Vol.I, by Schwartz & Perry, Interscience 1949 and 'Surface Active Agents' Vol.II by Schwartz, Perry & Berch 55 (Interscience 1958), in the current edition of "McCutcheon's Emulsifiers & Detergents" published by the McCutcheon division of Manufacturing Confectioners Company or in 'Tensid-Taschenbuch', H.Stache, 2nd Edn., Carl Hanser Verlag, Munchen & Wien, 1981.

In the case of the primary surfactants, suitable nonionic types includes in particular the reaction

products of compounds having a hydrophobic group and a reactive hydrogen atom, for example aliphatic alcohols, acids, amides or alkyl phenols with alkylene oxides, especially ethylene oxide either alone or with propylene oxide. Specific nonionic detergent compounds are alkyl (C₆-C₁₈) primary or secondary linear or branched alcohols with ethylene oxide, and products made by condensation of ethylene oxide with the 5 reaction products of propylene oxide and ethylenediamine. Other so-called nonionic detergent compounds include long chain tertiary amine oxides, long chain tertiary phosphine oxides and dialkyl sulphoxides.

The primary anionic detergent surfactants are usually water-soluble alkali metal salts of organic sulphates and sulphonates having alkyl radicals containing from about 8 to about 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher acyl radicals. Examples of suitable synthetic anionic 10 detergent compounds are sodium and potassium alkyl sulphates, especially those obtained by sulphating higher (C₈-C₁₈) alcohols produced for example from tallow or coconut oil, sodium and potassium alkyl (C₉-C₂₀) benzene sulphonates, particularly sodium linear secondary alkyl (C₁₀-C₁₅) benzene sulphonates; sodium alkyl glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow or 15 coconut oil and synthetic alcohols derived from petroleum; sodium coconut oil fatty monoglyceride sulphates and sulphonates; sodium and potassium salts of sulphuric acid esters of higher (C₈-C₁₈) fatty alcohol-alkylene oxide, particularly ethylene oxide, reaction products; the reaction products of fatty acids such as coconut fatty acids esterified with isethionic acid and neutralised with sodium hydroxide; sodium and potassium salts of fatty acid amides of methyl taurine; alkane monosulphonates such as those derived by reacting alpha-olefins (C₈-C₂₀) with sodium bisulphite and those derived from reacting paraffins with SO₂ 20 and Cl₂ and then hydrolysing with a base to produce a random sulphonate; and olefin sulphonates, which term is used to describe the material made by reacting olefins, particularly C₁₀-C₂₀ alpha-olefins, with SO₃ and then neutralising and hydrolysing the reaction product. The preferred anionic detergent compounds are sodium (C₁₁-C₁₅) alkyl benzene sulphonates and sodium (C₁₆-C₁₈) alkyl sulphates.

It is also possible to include, as a primary surfactant, an alkali metal soap of a fatty acid, especially a 25 soap of an acid having from 12 to 18 carbon atoms, for example oleic acid, ricinoleic acid, and fatty acids derived from castor oil, rapeseed oil, groundnut oil, coconut oil, palmkernel oil or mixtures thereof. The sodium or potassium soaps of these acids can be used, the potassium soaps being preferred.

The compositions also contain electrolyte in an amount sufficient to bring about structuring of the 30 detergent active material. Preferably though, the compositions contain from 1% to 60%, especially from 10 to 45% of a salting-out electrolyte. Salting-out electrolyte has the meaning ascribed to in specification EP-A, 79 646. Optionally, some salting-in electrolyte (as defined in the latter specification) may also be included, provided if of a kind and in an amount compatible with the other components and the composition is still in 35 accordance with the definition of the invention claimed herein. Some or all of the electrolyte (whether salting-in or salting-out), or any substantially water insoluble salt which may be present, may have detergency builder properties. In any event, it is preferred that compositions according to the present invention include detergency builder material, some or all of which may be electrolyte. The builder material is any capable of reducing the level of free calcium ions in the wash liquor and will preferably provide the composition with other beneficial properties such as the generation of an alkaline pH, the suspension of soil removed from the fabric and the dispersion of the fabric softening clay material.

40 Examples of phosphorous-containing inorganic detergency builders, when present, include the water-soluble salts, especially alkali metal pyrophosphates, orthophosphates, polyphosphates and phosphonates. Specific examples of inorganic phosphate builders include sodium and potassium tripolyphosphates, phosphates and hexametaphosphates.

Examples of non-phosphorus-containing inorganic detergency builders, when present, include water- 45 insoluble alkali metal carbonates, bicarbonates, silicates and crystalline and amorphous aluminosilicates. Specific examples include sodium carbonate (with or without calcite seeds), potassium carbonate, sodium and potassium bicarbonates, silicates and zeolites.

Examples of organic detergency builders, when present, include the alkaline metal, ammonium and substituted ammonium polyacetyl carboxylates and polyhydroxysulphonates. Specific examples include 50 sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylenediaminetetraacetic acid, nitrilotriacetic acid, oxydisuccinic acid, melitic acid, benzene polycarboxylic acids, citric acid, tartrate disuccinic acid and tartrate mono-succinic acid.

Apart from the ingredients already mentioned, a number of optional ingredients may also be present, for example lather boosters such as alkanolamides, particularly the monoethanolamides derived from palm 55 kernel fatty acids and coconut fatty acids, fabric softeners such as clays, amines and amine oxides, lather depressants, oxygen-releasing bleaching agents such as trichloroisocyanuric acid, inorganic salts such as

sodium sulphate, and, usually present in very minor amounts, fluorescent agents, perfumes, enzymes such as proteases and amylases, germicides and colourants.

The invention will now be illustrated by way of the following Examples.

5

Example 1: Salting-out Resistance of Surfactants

	Active detergent	Salting-out Resistance	
		Amount of NTA to get phase separation at room temperature of a 5% w/w surfactant solution	
		grams NTA added to 200 ml surfactant solution	grams equivalent added to 1 litre surfactant solution
15			
20	Ethoxylated fatty alcohol, $C_{12-15}E_7$	18.5-22	1.0-1.2
	Alkyl ether sulphate, LE_3S	59	3.2
	" " " LE_5S	74	4.0
25	" " " LE_6S	59	3.2
	" " " LE_8S	48	2.6
	Alkyl ether carboxylate, $LE_2.5C$	59	3.2
	" " " $LE_4.5C$	94	5.1
	" " " LE_6C	98	5.3
30	" " " LE_8C	106	5.8
	" " " $LE_{10}C$	106	5.8
	Alkyl ether phosphate, $C_{12-15}E_5P$	118	6.4
	" " " $C_{12-15}E_{10}P$	140	7.6
35	Alkyl ether sulphonate, $LE_{2.2}SC$ di sodium salt	> ca 180*	> ca 9.5*
	Alkyl dimethyl amine oxide, LAO	116	6.3
	Di C_{10} diphenyloxide disulphonate = Dowfax 3B2 ex Dow	170	9.2
40	Alkyl polyglucoside, $C_{8-10}G_{2-6}$ Triton CG-110	> ca 180*	> ca 9.5*
45	Alkyl polyglucoside Triton BG-10	> ca 180*	> ca 9.5*

50

55

	Active detergent	Salting-out Resistance	
		Amount of NTA to get phase separation at room temperature of a 5% w/w surfactant solution	
		grams NTA added to 200 ml surfactant solution	grams equivalent added to 1 litre surfactant solution
10	Alkyl polyglucoside , C ₉₋₁₁ G ₁	97	5.3
15	" " " C ₉₋₁₁ G ₃	> ca 180*	> ca 9.5*
	" " " C ₁₂₋₁₃ G ₁	0	0
	" " " C ₁₂₋₁₃ G ₃	> ca 180*	> ca 9.5*

20 C_x x = alkyl chain length
 L_x = Lauryl
 S = Sulphate
 E_y = Ethylene oxide chain length
 C_y = Carboxylate
 P = Phosphate
 G = Glucoside units
 * = saturated with NTA.

25

30

35

40

45

50

55

Example 2

Surfactant molecules ranked in order of their Salting-out Resistance.

Active detergent	SOR g.equiv NTA/litre
Alkyl polyglucoside, $C_{12-13}G_1$	0
Ethoxylated fatty alcohol, $C_{12-15}E_7$	1.0 - 1.2
Alkyl ether sulphate, LE_8S	2.6
" " " LE_3S	3.2
" " " LE_6S	3.2
Alkyl ether carboxylate, $LE_{2.5}C$	3.2
Alkyl ether sulphate, LE_5S	4.0
Alkyl ether carboxylate, $LE_{4.5}C$	5.1
" " " LE_6C	5.3
Alkyl poly glucoside, $C_{9-11}G_1$	5.3
Alkyl ether carboxylate, LE_8C	5.8
" " " $LE_{10}C$	5.8
Alkyl dimethyl amineoxide, LAO	6.3
Alkyl ether phosphate, $C_{12-15}E_5P$	6.4
" " " $C_{12-15}E_{10}P$	7.6

	Active detergent	SOR g.equiv NTA/litre
5	Di-C ₁₀ diphenyloxide disulphonate	9.2
	Alkyl ether sulphosuccinate, LE _{2.2} SC	> 9.5
10	Alkyl poly glucoside, C ₈₋₁₀ G ₂₋₆ " (Triton BG-10)	> 9.5 > 9.5
15	Alkyl poly glucoside, C ₉₋₁₁ G ₃ " " " C ₁₂₋₁₃ G ₃	> 9.5 > 9.5
20		
25		
30		
35		
40		
45		
50		
55		

Example 3

Maximum amount of dissolved electrolyte which can stably be incorporated in compositions with varying salting-out resistance of a cosurfactant.

Compositions:	Dodecyl Benzene Sulphonate Stabilising Surfactant	10% w/w	Water NTA	90% w/w added on top
Co-Surfactant				
	SOR, expressed in gram equiv- alents NTA added to 1 litre	Maximum amount of NTA which can be stably incorporated at various cosurfactant/DOBS ratio (w/w). (8 NTA added on top)		
			8/2	6.5/3.5
				5/5
Ethoxylated fatty alcohol, C ₁₂ -15E ₇	1.0 - 1.2	0	0	0
Alkyl ether sulphate, LE ₃ S	3.2	27	27	27
Alkyl ether carboxylate, LE _{4.5} C	5.1	38	36	32
Alkyl ether phosphate, C ₁₂ -15E ₅ P	6.4	>42*	39	>32
Alkyl poly glucoside, C ₁₂ -13G ₃	> ca. 9.5	>42*	>42*	>42*

* saturated

This table demonstrates: the higher the SOR of the cosurfactant, the more soluble salt can stably be incorporated in liquid detergent formulations.

55	50	45	40	35	30	25	20	15	10	5
----	----	----	----	----	----	----	----	----	----	---

Example 4

Maximum amount of dissolved electrolyte which can stably be incorporated in compositions with varying salting-out resistance of the surfactant.

Compositions:	DoBS or C ₁₂₋₁₅ E ₅ P Ethoxylated fatty alcohol, C ₁₂₋₁₅ E ₇	10 ⁸	Water	90% added NTA on top
Surfactant	SOR, expressed in gram equiv- alents NTA added to 1 litre	Maximum amount of NTA which can stably be incorporated at various surfactant/C ₁₂₋₁₅ E ₇ (w/w) ratio. (8 NTA added on top).		
DoBS	0.2*	0	12	4/6
Alkyl ether phosphate, C ₁₂₋₁₅ E ₅ P	6.4	>35	>35	>35

* estimated from phase diagrams

This table demonstrates that with strong salting-out resistant surfactant molecules, large amounts of soluble salt can be incorporated in liquid detergent formulations.

55 50 45 40 35 30 25 20 15 10 5

Example 5
Electrolyte tolerance of compositions containing co-surfactant with varying Salting Out Resistance.

Compositions:

Co-Surfactant	Dodecyl Benzene Sulphonate	Co-Surfactants	10% w/w	Water	90% w/w NTA added on top	Maximum amount of NTA which can be stably incorp- (% added on top)	Amount of maximum amount of NTA, i.e.: - <u>co-surfactant</u> <u>total-surfactant</u>
Alkyl ether carboxylate LE _{4.5} C				5.1	40	0.9	
Alkyl ether phosphate C ₁₂₋₁₅ E ₅ P				6.4	> ca 42*	0.8	
Alkyl ether sulphosuccinate LE _{2.2} SC				> ca 9.5	37	0.8	
Alkyl ether sulphoside C ₁₂₋₁₃ G ₃				> ca 9.5	> ca 42*	0.1	
Alkyl poly glucoside C ₁₂₋₁₃ G ₃							

This table demonstrates: At high levels of incorporated NTA (>30%), less cosurfactant is needed to obtain a stable liquid detergent on increasing salting-out resistance.

* saturated.

55	50	45	40	35	30	25	20	15	10	5
----	----	----	----	----	----	----	----	----	----	---

Example 6

Ternary active liquid detergent formulations containing salting-out resistant active molecules.

Co-surfactant	Compositions:		10% w/w	Water NTA 15, 25 or 35% w/w	Maximum weight fraction* of ethoxylated fatty alcohol (wrt total surfactant) which can be stably incorporated (wt fracn. DoBS bracketed)
	Dodecyl Benzene Sulphonate Ethoxylated fatty alcohol, C ₁₂₋₁₅ E ₇) Co-surfactant	Minimum weight fraction * of co-surfactant (wrt total surfactant) to obtain stable liquid- weight fracn. DoBS bracketed			
NTA Level	15% NTA	25% NTA	35% NTA	15% NTA	25% NTA
Alkyl ether sulphate, LE ₃ S	0.2 (0.6)	0.5 (0.5)	no stable	0.2 (0.6)	<0.1(0.5) 0
Alkyl ether carboxylate, LE _{4.5} C	0.1 (0.6)	0.3 (0.6)	systems	0.7 (0.3)	0.4 (0.3) <0.1(0.6) 0.1 (0.3)
Alkyl ether phosphate, C ₁₂₋₁₅ E ₅ P	0.1 (0.6)	0.4 (0.4)	0.4 (0.1)	0.5 (0.3)	0.4 (0.2) 0.6 (0.4)
Alkyl poly glucoside, C ₁₂₋₁₃ G ₃	0.1 (0.6)	0.2 (0.7)	0.2 (0.7)	0.4 (0.5)	0.2 (0.5) 0.2-0.3 (0.3)

* see also Fig.1.

This table demonstrates generally that on increasing salting-out resistance of the co-surfactant: (1) the amount of co-surfactant necessary to get a stable system is decreasing
(2) the amount of ethoxylated fatty alcohol which stably can be incorporated is increased.

Example 7

Ternary active liquid detergent formulations containing salting-out resistant active molecules

Compositions: Dodecyl Benzene Sulphonate)
Ethoxylated fatty alcohol, C₁₂-15E₇) 23% w/w
)
Co-surfactant

Stabilising surfactant

Minimum weight fraction* of co-surfactant (wrt total surfactant) to obtain a stable liquid-weight frac. DOBS bracketed

Na citrate level	10% citrate	15% citrate	10% citrate	15% citrate
Alkyl ether sulphate, LE ₃ S	0 ⁺	0.2 (0.7)	0.3 (0.5)	0.1 (0.7)
Alkyl poly glucoside, C ₁₂ -13G ₃	0 ⁺	0.1 (0.7)	0.4 (0.5)	0.3 (0.5)

* see also Fig. 1

+ also stable compositions without cosurfactant.

This table demonstrates the same phenomena as Example 6.

55 50 45 40 35 30 25 20 15 10 5

Example 8

Ternary active liquid detergent formulations containing salting-out resistant molecules.

Compositions: Dodecyl Benzene Sulphonate
Ethoxylated fatty alcohol, C₁₂₋₁₅E₇ or C₁₂₋₁₅E₃
Co-surfactant

Ethoxylated fatty alcohol	Co-surfactant	Maximum weight fraction* of nonionic detergent (wrt total surfactant level) which can be stably incorporated	Remarks
C ₁₂₋₁₅ E ₇	None	0.3 (1) 0.7/0.3/- **	* see also Fig. 1
"	LE ₃ S	0.3 (3) 0.7/0.3/-	(1) Ethoxylated fatty alcohol only
"	LE _{4.5} C	0.3 (3) 0.7/0.3/-	(2) Ethoxylated fatty alcohol plus Alkyl poly glucoside
"	C ₁₂₋₁₅ E ₅ P	0.3 (3) 0.7/0.3/-	(3) Ethoxylated fatty alcohol only!
"	C ₁₂₋₁₃ G ₃	0.6 (2) 0.4/0.3/0.3	co-surfactant does not lead to increased level of nonionic detergent
C ₁₂₋₁₅ E ₃	None	0.4 (1) 0.6/0.4/-	** wt ratio DoBS/ethoxylated fatty alcohol/ co-surfactant
"	C ₁₂₋₁₃ G ₃	>0.5 (2) 0.5/0.3/0.2	

It is believed that with stabilising surfactant molecules which are nonionic in character (C₁₂₋₁₅E₃) stable formulations with a high proportion of nonionic surfactants can be formed.

Example 9

5 Demonstration of breakdown of a lamellar phase (and consequently no stabilisation of the corresponding detergent) when replacing C₁₂₋₁₅E₇ by C₁₃₋₁₅E₂₅ (in whole or in part).

10 Compositions: Surfactants 10% w/w
NTA 15% w/w
Water 75% w/w

15	LAS	Co-Surfactant			Phases ⁴⁾	Stability
		C ₁₂₋₁₅ E ₇	LE ₃ S ¹⁾	C ₁₂₋₁₅ E ₅ P ²⁾		
16	6	4	-	-	-	L ₁ +LAM Unstable
17	6	3	1	-	-	L ₁ +LAM Unstable
18	6	3	-	1	-	L ₁ +LAM Stable
19	6	3	-	-	1	L ₁ +LAM Unstable
20	6	2	2	-	-	L ₁ +LAM Stable
21	6	2	-	2	-	L ₁ +LAM Stable
22	6	2	-	-	2	L ₁ +L ₂ + LAM Unstable
23	6	1	3	-	-	L ₁ +LAM Stable
24	6	1	-	3	-	L ₁ +LAM Stable
25	6	1	-	-	3	L ₁ +L ₂ + LAM Unstable
26	6	-	4	-	-	L ₁ +LAM Stable
27	6	-	-	4	-	L ₁ +LAM Stable
28	6	-	-	-	4	L ₁ +L ₂ Unstable

SOR in g eq. NTA to 1 litre

35 1) 3.2 2) 6.4 3) 2.1

4) Phases:

L₁ = active-poor isotropic phase

L₂ = active-rich isotropic phase

LAM = Lamellar Liquid crystalline phase.

45 NOTE:- When replacing C₁₂₋₁₅E₇ by more salting-out resistant surfactants, this may only lead to stabilisation when the lamellar phase (LAM) is not broken down to an active rich isotropic phase (L₂). This breakdown is demonstrated using C₁₃₋₁₅E₂₅.

50

55

Claims

1. An aqueous liquid detergent composition comprising detergent active material and dissolved electrolyte in amounts sufficient to result in a surfactant structure within said composition, which composition yields substantially no clear liquid active rich layer upon centrifuging at 750G for 20 hours at 25°C, wherein the detergent active material comprises a stabilising surfactant, which has an average alkyl chain length greater than 6 C-atoms, and which has a salting-out resistance, greater than, or equal to 6.4.
2. A composition according to claim 1, wherein the detergent active material also comprises a nonionic surfactant and/or a non-alkoxylated anionic surfactant and/or an alkoxylated anionic surfactant.
3. A composition according to either preceding claim, wherein the stabilising surfactant is selected from:-
alkyl polyalkoxylated phosphates;
alkyl polyalkoxylated sulphosuccinates;
dialkyl diphenyloxide disulphonates;
- 15 alkyl polysaccharides;
and mixtures thereof.
4. A composition according to any preceding claim, wherein the stabilising surfactant, or at least one of the stabilising surfactants has a salting-out resistance greater than or equal to 9.0.
5. A composition according to any preceding claim, wherein the stabilising surfactant has an average alkyl chain length greater than 8 carbon atoms.
- 20 6. A composition according to any preceding claim, wherein the detergent active material constitutes from 2% to 50% by weight of the total composition.
7. A composition according to any preceding claim, wherein the stabilising surfactant constitutes from 0.1% to 45% by weight of the total composition.
- 25 8. A composition according to any preceding claim, wherein the stabilising surfactant constitutes from 5% to 90% by weight of the detergent active material.
9. A composition according to any preceding claim, wherein the composition comprises from 1 to 60% by weight of a salting-out electrolyte, all or part of which constitutes said dissolved electrolyte.
10. A composition according to claim 9, wherein the salting-out electrolyte constitutes from 10 to 45% by weight of the total composition.
- 30 11. A composition according to any preceding claim, which yields no more than 2% by weight phase separation upon storage at 25°C for 21 days from the time of preparation and has a viscosity no greater than 1 Pas at a shear rate of 21s⁻¹.

35

40

45

50

55



Neu eingetragen
Nouvellement déposé

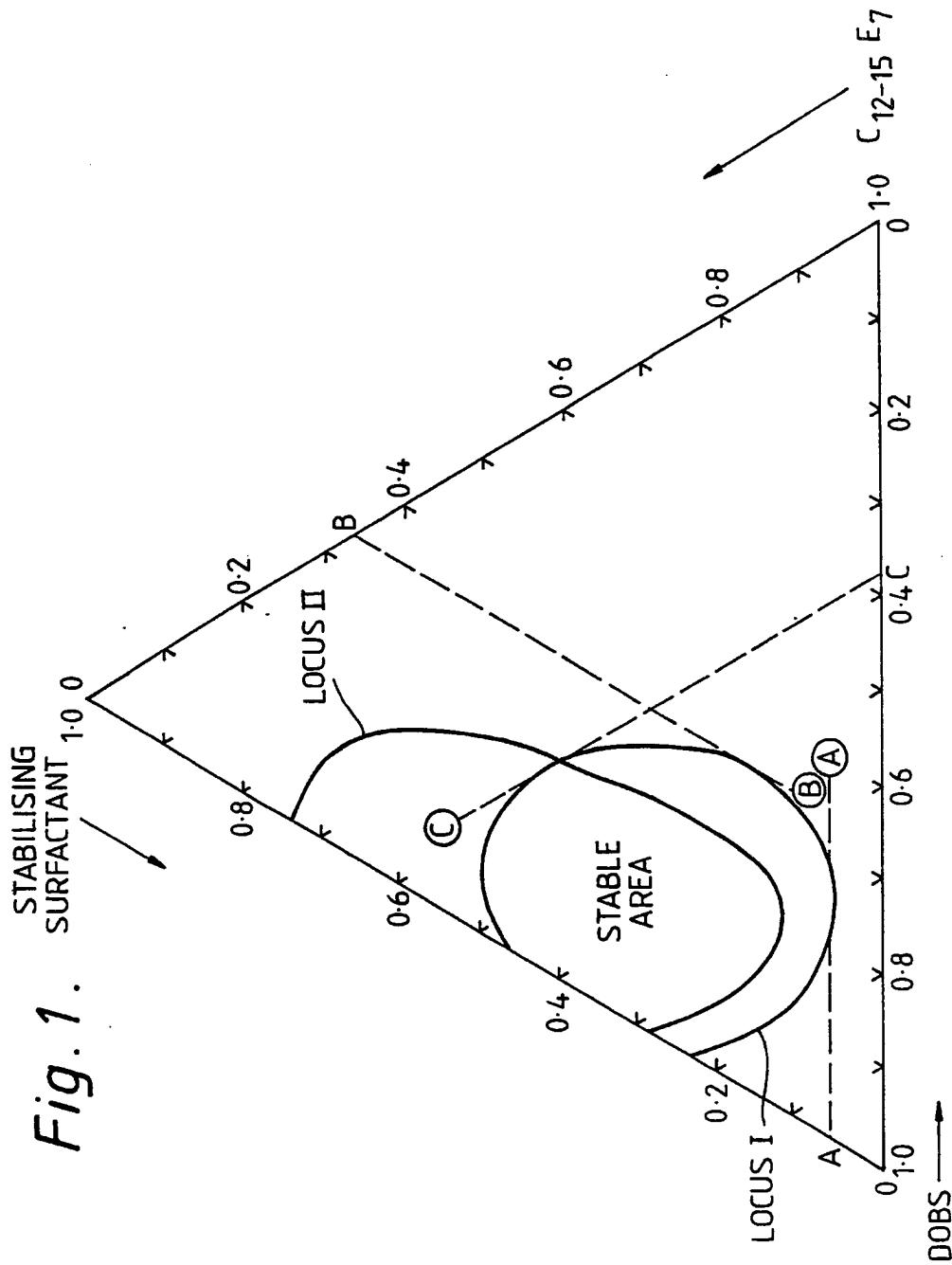
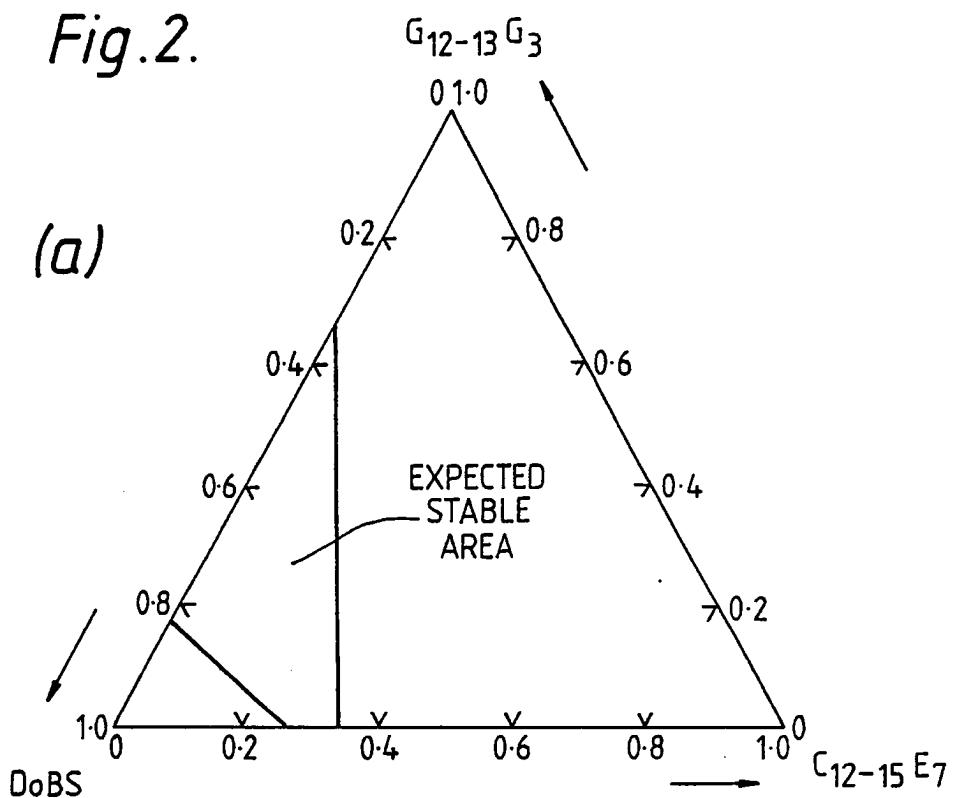


Fig. 2.

(a)



(b)

